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Novel adsorption materials based on graphene oxide/Beta zeolite composite materials and their adsorption performance for rhodamine B

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A B S T R A C T

In this paper, we developed an adsorption composite materials based on the incorporation of zeolite and graphene oxide (GO), which could significantly hoist the adsorption capacity of zeolite and improve the separation trouble of GO with outstanding adsorption ability. The GO/Beta zeolite (GB) composite materials with different GO contents were hydrothermally prepared by grafting the GO onto acid-treated Beta zeolite. The structure and physical properties of the GB composite materials were determined by a series of characterizations such as XRD, SEM, FTIR, Raman, BET and XPS. It was concluded that the GB composite materials were of the hierarchical porous structure and GO nanosheets were bonded onto the active surface of Beta zeolite. The adsorption capacity of the GB composite materials was examined by the adsorption of RB dye molecular from aqueous solution. Moreover, the effect of adsorption conditions on the adsorption of RB onto the GB composite materials for rhodamine B (RB) was extensively investigated. Finally, the adsorption behaviors of the GB composite materials for RB were fitted by Langmuir isotherm and Freundlich isotherm equations, respectively. The result showed that the maximum adsorption capacity of the GB composite materials was up to 64.47 mg/g.

1. Introduction

Rhodamine B (RB) is a typical industrial dye used mainly in textile, plastic, leather, dyeing, paper, and printing industries [1,2]. From health and hygiene points of view, it is carcinogenic and causes irritation, redness and pain in the eyes and skin, respectively. It is known that about 15% of the dyes are lost in wastewater during dyeing operation [3]. Therefore, in industrial practices, it is imperative to remove RB from the effluents before discharging back to nature.

Adsorption was considered to be cost-effective and efficient for removing dyes, heavy metals and other organic and inorganic hazardous impurities from aqueous solutions. So, adsorption technique was frequently chosen the separation process [4,5]. Zeolites have already found many applications because of their many advantages, such as easy regeneration, low cost, green environmental protection, thermal stability, high cation-exchange capacity and larger surface area [6]. Beta zeolite as a kind of synthetic zeolite is one of the most widely used molecular sieves due to being of many important characteristics, such as large pores, high Si/Al ratio and three dimensional pore networks [7]. Particularly in adsorption, Beta zeolite exhibited a promising prospect. For example, the maximum adsorption capacity of beta zeolite for Pb^{2+} was 2.5 meq/g [8]. Fu et al. [9] reported the removal of thiophene and quinoline by CaY/beta and CeY/beta composites. Ma et al. [10] studied the adsorption of n-butane onto Beta/MCM-41 composite materials.

Graphene oxide (GO) had a strong propensity to interact with positively charged species such as metal ions and dyes. Recently, GO and GO composite materials have become a hot spot in adsorption research. Yu Yang et al. [11] reported that the adsorption capacity of GO-modified zeolite attained 55.56 mg/g. Tan L et al. [12] reported that the maximum adsorption capacity of GO for Cs (I) from water was 32.53 mg/g. Jin et al. [13] reported that the maximum adsorption capacities of magnetic rGOs at pH 6.5 and 293 K were 63.96 and 48.74 mg/g for 4-n-NP and BPA, respectively. Peng et al. [14] reported the adsorption of methylene blue (MB) onto GO, the experimental adsorption capacity of which was up to 2255.35 mg/g. Regretfully, although the adsorption capacity of GO is strong, it was regularly found to being difficult to separate from

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aqueous solution and faced to the most forefront environmental problems due to own potential toxicity and environmental behavior [15]. Fan Q et al. [16] reported that the new three-dimensional composite of polyaniline (PANI) and GO was synthesized by in-situ polymerization technique, and the maximum adsorption capacity of Hg (II) on PANI/GO from aqueous solution can achieve as high as 80.7 mg/g. The GO/carbon nanotubes composites (G-CNTs) were prepared by hydrothermal method, and the adsorption of methylene blue on G-CNTs was up to 81.97 mg/g [17].

In order to improve the adsorption capacity of Beta zeolite and solve the separation trouble of GO from aqueous solution, this paper fabricated a novel adsorption materials based on the combination of GO and Beta zeolite (GB). GO nanosheets were coated onto the surface of Beta zeolite by using GO aqueous solution under hydrothermal synthesis. The structure and properties of the composite materials with different GO contents were confirmed by a series of characterizations. The effect of the adsorption conditions on the adsorption capacity of RB onto the GB composite materials was extensively investigated. Finally, the adsorption isotherms of the composite materials for RB adsorption were explored.

2. Materials and methods

2.1. Chemicals and reagents

Rhodamine B (molecular weight 479.01 g/mol, CAS:81-88-9). Hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co.Lid (China). The GO dispersed aqueous solution (0.69 wt%) was prepared without undergoing dry procedure by improved Hummers' method [18]. After drying, the average size of GO powder was measured about 2–5 μm and the BET surface area was about 48 m^2/g. Beta zeolite (chemical composition: 90.07% SiO_2, 8.31% Al_2O_3, 0.065% P_2O_5, 1.47% Na_2O, 0.043% CaO, 0.017% Fe_2O_3, 0.019% K_2O) was synthesized by hydrothermal synthesis method with template-assisted fabrication [19]. All aqueous solutions were prepared using deionized water.

2.2. Acid treatment of Beta zeolite powder

Initially, 0.5 g Beta powder was suspended in 20 mL of deionized water. Then, 0.1 mL 32 wt% of aqueous hydrochloric acid was dropwisely added into and stirred the suspension for 30 min. Finally, the resulting acid-treated Beta powder was separated via centrifugation at 3000 rpm for 5 min, and followed by successive washing and centrifugation with deionized water.

2.3. Functionalization of acid-treated Beta zeolite with GO nanosheets

Firstly, the GO dispersion was added into the acid-treated Beta powder solution (0.05 g/mL). Then, the suspension was sonicated for 10s, stirred for 30min and then placed in an oven at 110 °C for 12 h. Finally, the residual powders were cooled down for further use. The final samples were marked as GB-1 (1 wt%), GB-2 (2 wt%) and GB-3 (6 wt%), respectively.

2.4. Characterizations

XRD patterns were obtained with D8 Advance X-ray diffraction (Bruker-AXS, Germany). SEM images were recorded by S-4800 Scanning Electron Microscope (Hitachi, Japan). FT-IR spectra were recorded on a IFS66/S type micro-infrared spectrometer (Varian, America). Raman measurements were carried out on spectroscopy instrument (Renishaw, England) using a 532 nm laser with a maximum power of 60 mW. BET specific surface areas were determined by nitrogen adsorption using Sorptomatic 1990 Thermo Finningen instrument (Thermo, America). XPS was recorded by ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific, America).

2.5. Adsorption experiments

In order to investigate the adsorption behavior of the Beta, GB-1, GB-2 and GB-3, the above as-prepared adsorbents (0.01 g) were dispersed in each of the standard aqueous RB aqueous solution (10 mL). The effect of adsorption time, pH value, adsorption temperature and initial RB concentration on adsorption capacity of RB onto the composite materials was explored. After the ending, the suspensions were filtered through a 0.45 μm membrane filter and the filtrate were analyzed using a UV–visible spectrophotometer at a wavelength of 354 nm. The RB concentrations were then calculated from a calibration curve. Hydrochloric acid and sodium hydroxide were used to control the pH value of each suspension.

The RB adsorption capacity q (mg/g) is calculated from Eq.

$$q = \frac{(C_0 - C)V}{W} \tag{1}$$

where C_0 and C are the initial and equilibrium concentration of RB (mg/L), respectively; V is the volume of the solution (L) and W is the dry mass of the adsorbent (g).

The recycling performance (η) of GB composite material was calculated from Eq.

$$\eta = q_n/q \times 100\% \tag{2}$$

where q_n and q are the adsorption capacity after the n-th time recycling and the initial adsorption capacity.

3. Results and discussion

3.1. Characterizations of GO/Beta composite materials

Fig. 1 shows the XRD patterns of GO, Beta and GB composite materials. GO nanosheets have a strong and broad diffraction peak at 2θ = 9.8°, which is due to the presence of oxygen functionalities in the basal plane of natural graphite [20]. The peaks around at 2θ = 7.8° and 22.3° indicate that the as-prepared zeolites are of BEA

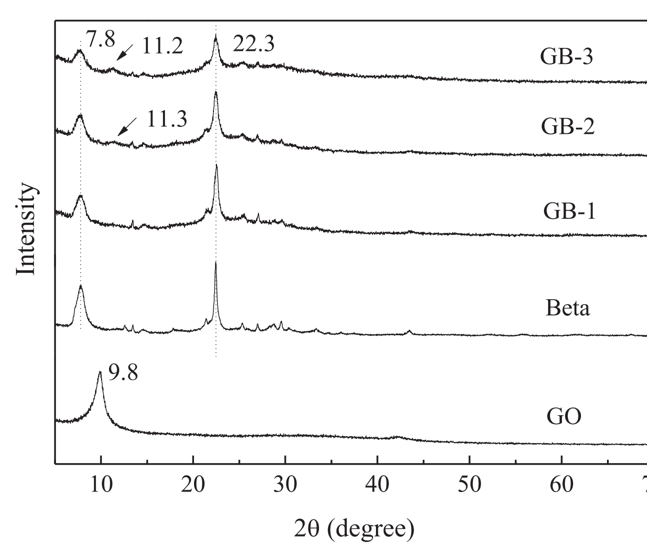

Fig. 1. XRD patterns of GO, Beta, GB-1, GB-2 and GB-3.